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Synchrotron tts - μ XRD identification of secondary phases in ancient ceramics

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Abstract

The study of the alteration process, and in particular of secondary phases precipitated in pottery after its production, can constrain the post-depositional environments or the type of use of the pottery. Detailed study of secondary phases can be done using different approaches, based on microscopic, microstructural and microchemical analyses, as well as mineralogical methods. In the present study are reported the results of the application of punctual mineralogical analysis by synchrotron through-the-substrate microdiffraction (tts - μ XRD) to analyse secondary phases precipitated in ancient pottery (Bronze Age pottery from Frattesina in Italy and Mesolithic pottery from Al Khiday in Sudan). Although the chemical composition of these secondary phases in many cases almost matches with the stoichiometric composition of a known mineral, only some of them were actually true mineral phases (i.e. with crystallinity and therefore showing diffraction peaks), while others were amorphous. Some phases, the occurrence of which was previously attested only on the basis of their chemical composition (determined by scanning electron microscope or the electron microprobe analysis), were univocally identified as true vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) and crandallite ($CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$) minerals. Part of the phases detected in studied pottery, the chemical composition of which was consistent with specific mineral phases, were instead amorphous. The synchrotron through-the-substrate microdiffraction (tts - μ XRD), therefore, represents a valid method for properly determine the mineralogical nature of secondary phases in pottery, as well as other small-sized and rare mineral phases occurring in polycrystalline materials of archaeological interest, such as pottery, mortars, painting and glassy materials.

Keywords: Mineralogy, Synchrotron through-the-substrate microdiffraction (tts - μ XRD), Vivianite, Crandallite, Amorphous phases, Secondary phases, Pottery

Introduction

Secondary phases in archaeological ceramics represent the products of post-depositional processes or contamination related to the pottery use. The study of these phases can therefore supply important information on the physical–chemical conditions of the burial environment and its changes over the time [1–7], as well as the type of use of the pottery [8].

In most of the cases, secondary phases precipitate in voids of the pottery paste and are therefore located in specific and often sub-millimetric or even micrometric sites. They can crystallize and hence constitute a true mineral or precipitate in form of an amorphous phase.

Due to their small size and the fact that in most of the cases they occur in very little quantities, they cannot be effectively isolated from the ceramic body or mechanically concentrated for being individually investigated. Only local analytical techniques, such as microanalysis at the scanning electron microscope or at the electron microprobe, can be used to retrieve successfully their chemical composition. However, determination of their crystalline nature is more difficult, since the structural methods commonly used (X-ray powder diffraction: XRPD) require large amount of material compared with that available for the secondary phases that sometimes appear in pottery. The dilution effect of the ceramic body, for instance in the case of XRPD analysis, determines that the secondary mineral phases are, in most of the cases, under the detection limit of the technique. Only local mineralogical analysis, undertaken using techniques such

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as micro-Raman or micro-diffraction, can solve this problem. In the case of micro-Raman, the possibility of using a small analytical spot (around 1 micron) determines this technique to be very useful for the mineralogical determination at a micro scale, therefore also focusing on specific site within the materials. But the limited available database of Raman spectra represents an important limitation in the spectra interpretation, especially of uncommon mineral phases. Micro-diffractometric technique in reflection mode can be used to characterise small sized crystals as well as small areas of archaeological materials, but the investigation areas of these methods are in many cases quite large (around 50 micron) [9, 10].

The use of synchrotron through-the-substrate micro-diffraction (tts- μ XRD) was here applied to the study of secondary mineral phases of different composition (phosphates, silicates) identified in a series of archaeological ceramics from different periods (Mesolithic, Bronze age) and sites (Sudan, Italy). This technique allows to make punctual analysis in thin section, using a spot size of few micrometres and it has proven to be a useful for the study of cultural heritage materials to mineralogically characterize phases, small in size, occurring in the coatings as well as in the ceramic body of pottery [11–15]. The Bronze Age pottery from Frattesina (north-eastern Italy), the secondary mineral phases of which were previously characterised under microscopic, microstructural and microchemical points of view [6], was deliberately selected among other possible case studies, to evaluate the application of the tts- μ XRD for the mineralogical analysis of the secondary phases.

Materials and methods

A set of secondary phases in various types of pottery, already petrographically, microstructurally and microchemically characterised at the scanning electron microscope (SEM) and by electron microprobe analysis (EMPA) [5, 6, 16, 17] were analysed by synchrotron through-the-substrate microdiffraction (tts- μ XRD). In particular, the pottery here analysed comes from: (i) the Bronze Age site of Frattesina in north-eastern Italy (pottery samples FRCON34 and FRE48); and (ii) the Mesolithic occupation levels (~7000–5250 BC) of the archaeological sites of Al Khiday in central Sudan [18–24] (pottery samples 203 and 211). tts- μ XRD analysis was performed at the Material Science and Powder Diffraction beamline [25] at ALBA synchrotron facility (Cerdanyola del Vallès, Barcelona, Spain). This end-station is equipped with Kirkpatrick-Baez mirrors providing a monochromatic focused beam of $15 \times 15 \mu\text{m}$ (FWHM) size and a Rayonix SX165 CCD detector. Since the measurement is in transmission mode, the lateral resolution provided by this beam size is of the same order as the

thin-section thickness (25–30 μm) [26]. The energy used in the experiments was 29.2 keV ($\lambda = 0.4246 \text{ \AA}$). The sample-detector distance (180–250 mm) and the beam centre positions were calibrated from LaB_6 diffraction data measured at exactly the same conditions as the sample. The tts- μ XRD allows collection of data directly on the thin sections preserving the textural context and allowing local mineral phase identification and/or structure determination [15, 26–28]. Mineralogical composition was retrieved for the analysed areas using Sleve+ plugin within PDF4+ database (ICDD).

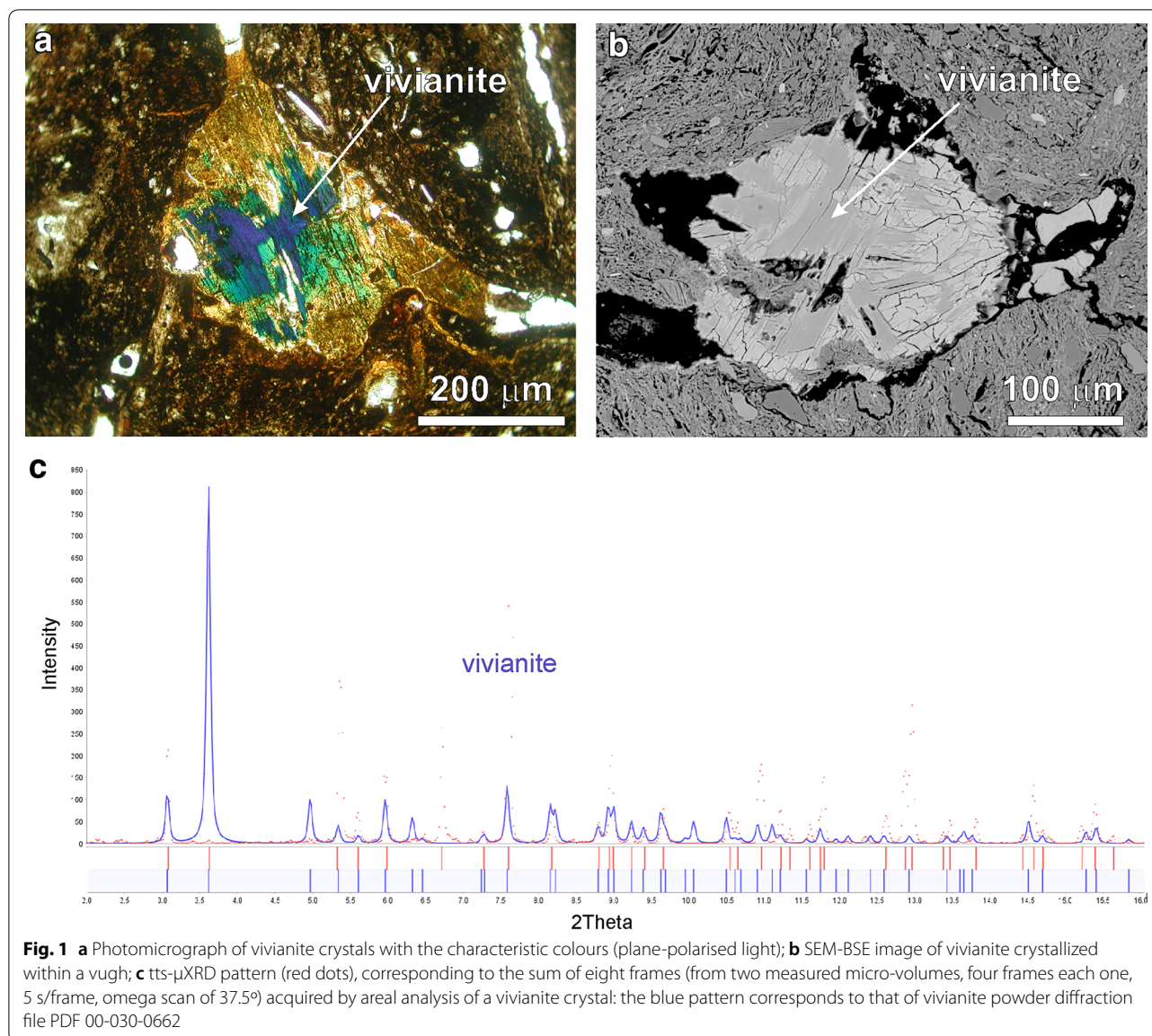
Results and discussion

The mineralogical analysis of the secondary phases observed in the studied samples shows that only some of them are crystalline, while others are amorphous.

The tts- μ XRD of crystals of iron phosphate (Fig. 1a, b), as microchemically determined by electron microprobe analysis in the Bronze age pottery from Frattesina [6], are mineralogically consistent with the diffraction pattern of vivianite $\text{Fe}_3(\text{PO}_4)_2 \cdot 8(\text{H}_2\text{O})$ (Fig. 1c). When the diffraction peaks of this phase are compared to those observed at the tts- μ XRD, it can be seen that some peak are missing. This is because the measured sample micro-volume contains only a single-crystal of vivianite. The sample was rotated during the measurement to increase the number of collected reflections but, due to the limited rotation range imposed by sample geometry, some regions of the reciprocal space could not be scanned. This determines that some reflections are missing and the intensities differ compared to the diffraction pattern of a polycrystalline sample. The pattern matching of vivianite is reported in Additional file 1: Fig. S1 and the list of Bragg reflections and their position after pattern matching of vivianite, as well as the refined unit cell parameters, in Additional file 1: Table S1.

Moreover, the detailed observation of the diffraction pattern of vivianite (Fig. 1c) show the occurrence of some peaks (low in intensity) such as at 2 Theta value of 6.71° , which does not find a correspondence with the reference pattern of vivianite (PDF file (00-030-0662)). The identification of the phase responsible of this peak was not possible due to the small number of reflexions.

Microscopically, vivianite crystals are characterised by prismatic habitus with good cleavage, pleochroism from pale yellow to deep cobalt blue and low birefringence (grey interference colours) (Fig. 1a). They are surrounded by a brown-yellowish phase (Figs. 1a, 2a), with a higher average atomic number in the scanning electron microscope-back scattered electron (SEM-BSE) image (Fig. 1b) and present irregular fractures. Despite the fact that the microchemical analysis at the EMPA of this phase [6] shows a stoichiometry corresponding to

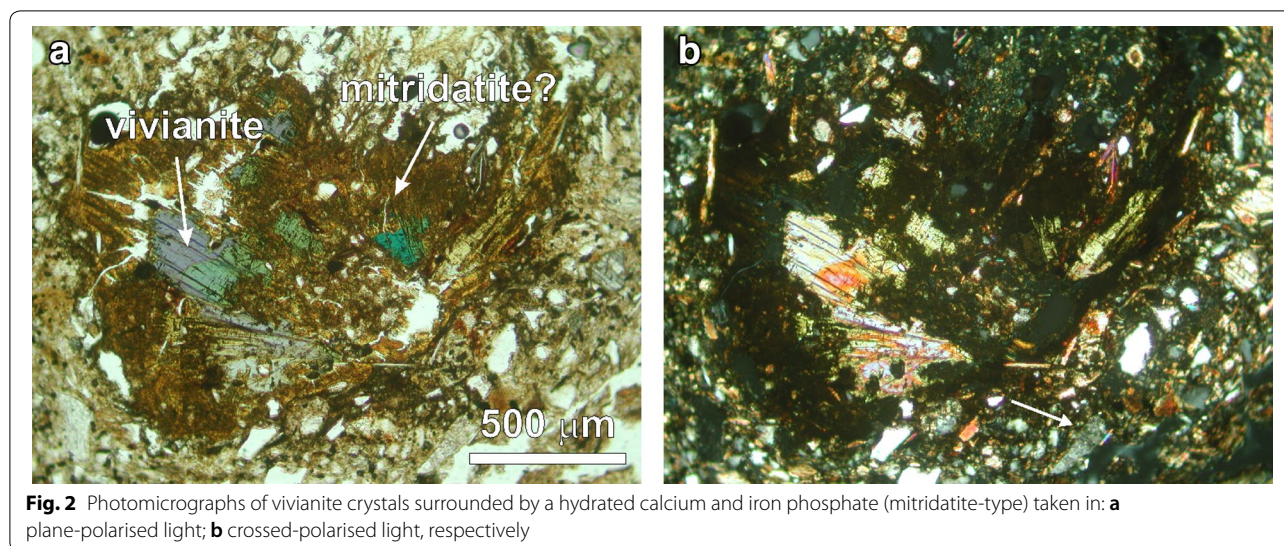


that of mitridatite $\text{Ca}_2\text{Fe}_3(\text{PO}_4)_3\text{O}_2 \cdot 3(\text{H}_2\text{O})$, the tts- μ XRD pattern indicated that this phosphate appears as amorphous in these samples. Since the preliminary test on this phase produced an amorphous signal, the scan was carried out in step mode (step scan without sample rotation) and the final diffraction pattern consists therefore on an amorphous signal. Two peaks with low intensity, were observed in the pattern and attributed to those of vivianite, which, according to Maritan et al. [6] and Maritan and Mazzoli [5], was the precursor phase of the mitridatite-type phosphate.

Bulk mineralogical analysis by XRPD of the Frattesina pottery detect only traces of phosphate, the broad peaks and very low intensity of which did not allow to the

definition of the mineralogical phases. The small size of these secondary precipitates and their occasional occurrence is also attested by the low concentration of P_2O_5 measured by X-ray fluorescence bulk chemical analysis (FRE48: 1.02 wt%; FRCON34: 0.69 wt%), which fall in the average values of other ceramic classes found in the region, in which none evidence of secondary phosphates were attested. Phosphates precipitated in these potsherds within both long channels (some hundreds microns in length) and small pores (some tens microns in size), forming geode-like structure, partially or completely filling the cavities.

As for the origin of the calcium and iron phosphate, the change in the burial environment, particularly the more



oxidising condition and the interaction with Ca-rich circulating ground water, promoted the transformation of vivianite into a hydrated calcium and iron phosphate. Mitridatite is in these samples not crystalline since it formed through an Ostwald step sequence after vivianite. In such situation, the transformation stopped at a higher Gibbs energy, with the amorphous particles characterised by a lower superficial energy than if the mitridatite were in crystalline form. Therefore, the transformation determined the formation of an amorphous phase with a chemical composition consistent with that of mitridatite, which could in fact eventually evolve to crystalline mitridatite. Both thermodynamic and kinetic factors influenced the transformation and inhibited the crystallization of mitridatite. The amorphous state of this secondary phase can be also observed from its optical behaviour (Fig. 2a, b) under a petrographic microscope, as the lack of interference colours is compatible with a cubic or, as it is the case, an amorphous phase. It is important to remark that the bulk mineralogical composition of the pottery obtained using conventional XRPD bearing these secondary phases does not comprise any phosphate [6], due to their low content and to the fact that only part of them (vivianite) is crystalline.

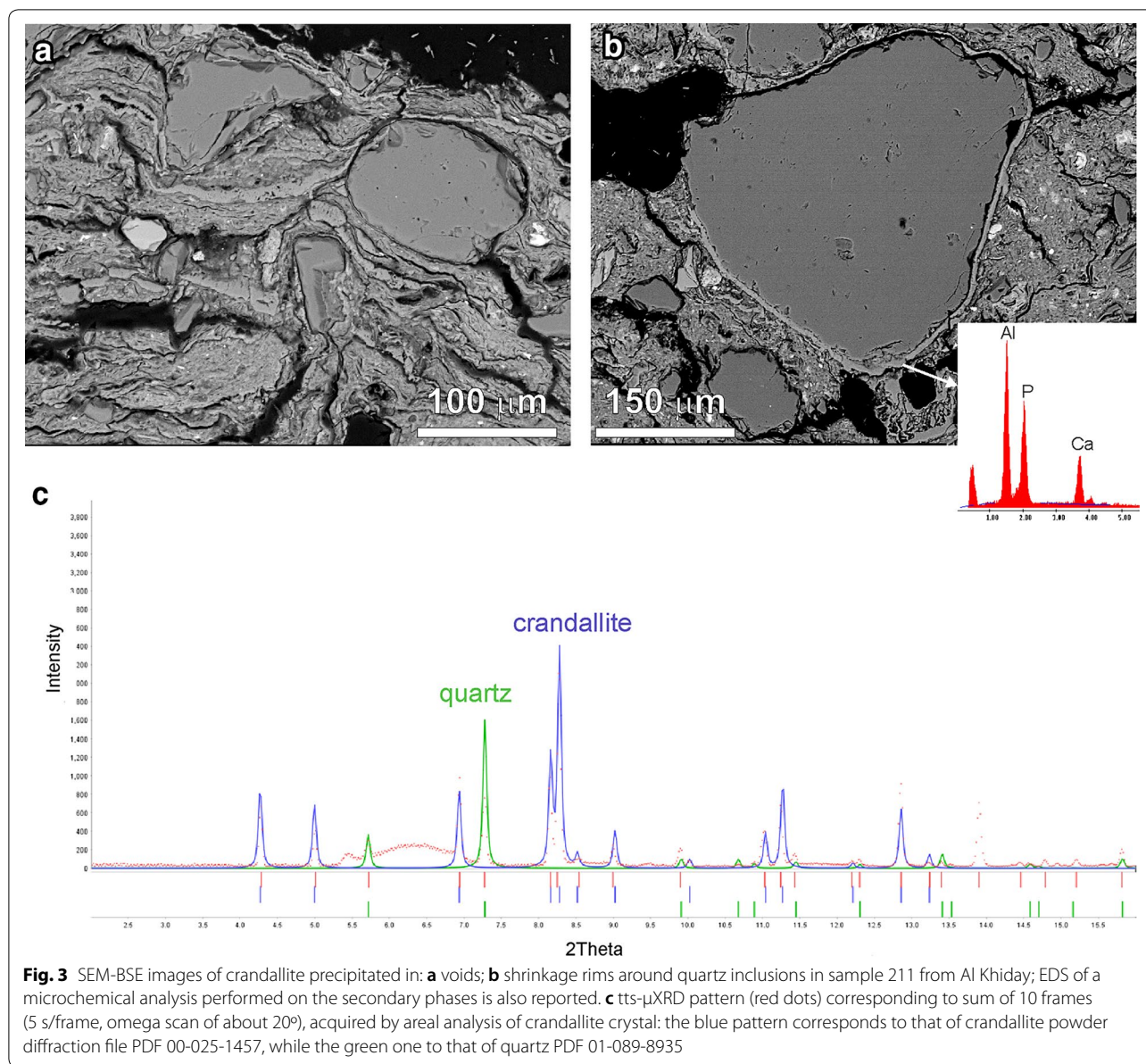
Vivianite and amorphous iron and calcium phosphate are post-depositional phases, precipitated in the pottery during the burial, according to the model proposed by Maritan et al. [6].

The microstructural analysis at the SEM of the Mesolithic pottery from Al Khiday [16, 17] pointed out that sample 211 contained, in the outer most portion, a secondary phase characterised by a higher average atomic number with respect to the surrounding matrix and quartz inclusions, being lighter grey in the SEM-BSE

images (Fig. 3a, b). This secondary phase precipitated in the open porosity, partially filling it with geode-like structures of acicular crystals (Fig. 3a, b), or forming a compact massive precipitate filling completely the pores. It is interesting to note that the microchemical analysis indicates that it corresponds to an aluminium and calcium phosphate (Fig. 3b), the diffraction pattern of which, obtained through the $tts\text{-}\mu\text{XRD}$, is consistent with that of crandallite $\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5\cdot\text{H}_2\text{O}$ (Fig. 3c). The additional presence of quartz in the diffraction pattern relates to the small size of the crandallite precipitate compared with that of the focused spot ($15 \times 15 \mu\text{m}$), which therefore comprised also quartz crystals occurring in the ceramic paste. The identification of crandallite is also consistent with the crystals observed under the petrographic microscope, with a very pale yellowish colour and low relief in plane-polarised light, and very low birefringence (grey interference colour) in crossed-polarised light.

The precipitation of this phase took place mainly on the elongated channels of the outermost portion of the inner surface of the pottery, up to about 1 mm in depth, and filling pores of thickness of some tens microns. This pottery is characterised by a pervasive pore system, mainly constituted by channels, planar voids and elongated vughs, as well as shrinkage rims around the quartz inclusions, covering about 20% of the total area according to image analysis determination [16].

Crandallite was previously attested as a secondary phase in Amazonian pottery but it was identified only on compositional grounds, no mineralogical evidence supported its occurrence [8]. In the present study, the possibility of performing the mineralogical analysis also on small-crystal aggregates by $tts\text{-}\mu\text{XRD}$, allowed to



univocally identify this secondary phase from a mineralogical viewpoint. In spite of the fact that a very large set of samples (more than 400 potsherds) from the archaeological sites of Al Khiday have been petrographically, microstructurally and chemically analysed [16, 17, 29], only in one of them (sample 211) it was possible to identify crandallite. This potsherd contains a higher percentage of P_2O_5 (1.82 wt%) than almost all the others produced with the same recipe (around 0.30 wt%), with the exception of few potsherds coming from the same area (site 10-W-4), in which the P_2O_5 range around 1.5–2 wt%. In all these samples with a high phosphorous content no phosphates were observed by X-ray powder diffraction

(XRPD) performed on the bulk. The microstructural analysis at the SEM indicated that only in sample 211 crandallite could have precipitated as an independent phase and μ XRD results confirm that the secondary phase is truly crandallite and not an amorphous precipitate. In all the other P-rich potsherds, phosphorous was probably adsorbed by the ceramic paste, without the precipitation an individualized secondary phase, according also to what previously observed by Freestone et al. [30] and Freestone [31]. Interestingly all the samples with high phosphorous content in Al Khiday come from the same site (10-W-4) dated to the Late Mesolithic (6000 to 5250 BC).

The presence of crandallite in the potsherd can be interpreted as a proof that the pot was used for cooking for a very long time. More specifically, phosphorous and calcium were probably supplied by the cooked meat, and in particular by the bones, mineralogically composed by hydroxylapatite. The experimental work of Rodrigues and Costa [32] supports this interpretation, in their work on the effect of phosphorous incorporation in cooking pots, variscite, another hydrated aluminium phosphate ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$), crystallized after a long time of contact with an experimental solution containing 0.03 wt% P_2O_5 and 0.03 wt% CaO (more than 600 h of cooking). Rodrigues and Costa experiments were performed using a solution and not real food, and the formed secondary phosphates were so abundant that could be observed by XRPD on the bulk [32]. In any case, their study clearly indicates that the accumulation and crystallization of secondary phosphates is time dependent. The crandallite found in sample 211 would have formed similarly: this phosphate would have crystallized after reaction between alumina and the phosphorous and calcium available in the cooking fluids. Alumina could come from the ceramic body, after the phyllosilicate decomposition (and in particular kaolinite, the breakdown of which determine at temperatures exceeding 550 °C the formation of a metastable and amorphous phase, metakaolin, a known source of alumina and silica). This site has been considered a seasonal occupation devoted to hunting activities, as inferred by analysis of faunal remains [19]. Cooking the meat, most probably stewing it, may have provided some advantages: softening muscle fibres, eliminating or reducing bacteria and pathogens, increasing

energy yields, longer preservation [33, 34]. The lack of crandallite in other samples from the same site may be explained by the use of the pottery for: (i) cooking other type of food than meat, such as vegetables and other plants; (ii) making few cooking, not enough to determinate the accumulation and precipitation of crandallite. A series of residues analysis (on about 100 potsherds) are at the moment under execution to define the type of lipids occurring in the pottery from Al Khiday. This on-going research is also coupled with a series of experimental cooking of different types of food and for varying duration (number of times that the pot is used), using locally produced pottery with analogous characteristic in terms of ceramic paste.

Another secondary phase was found and analysed on another potsherd (sample 203) from the same site at Al Khiday. A large deposit laid down in the inner surface of the potsherd (Fig. 4a) and did not entered the open porosity even in the outermost portion of the ceramic. A detailed analysis indicates that it is formed by a very dense material, in some parts showing thin plate-like shape (Fig. 4b), with a chemical composition corresponding to that of a silicate containing calcium, sodium, aluminium and magnesium (Fig. 4b). The μXRD of this crust reveals that it is not crystalline.

Considering the shape of the portion, the high content of silicon, as well as the amorphous state, this deposit could be interpreted as the product of precipitation of amorphous silica enriched in impurities. According to the experimental work by Wang et al. [35], magadiite, a hydrous sodium silicate phyllosilicate ($\text{NaSi}_7\text{O}_{13}(\text{OH})_3 \cdot 4(\text{H}_2\text{O})$), precipitates from a hydrous

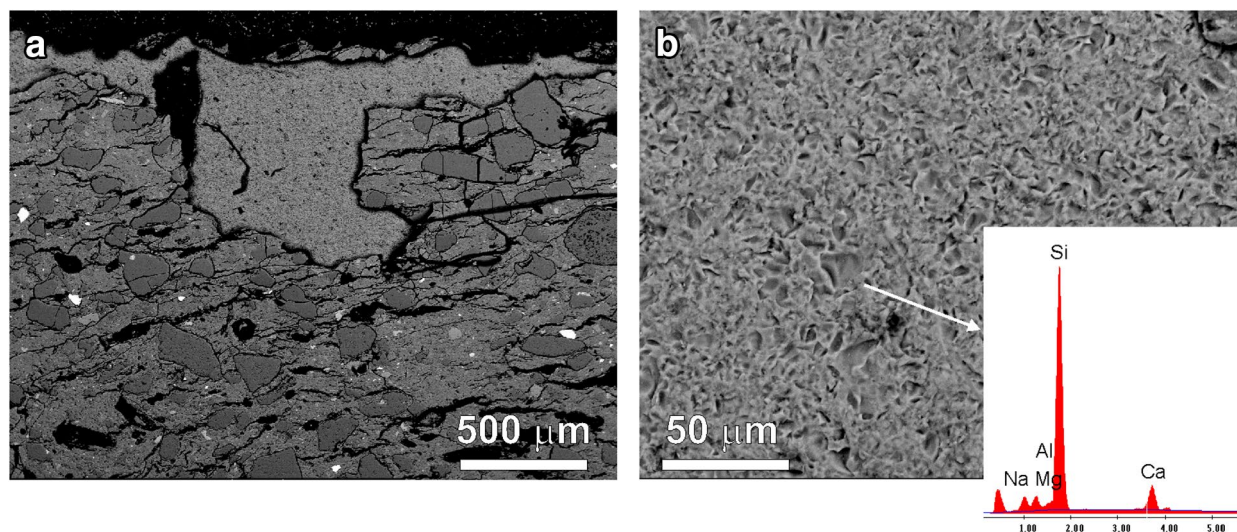


Fig. 4 SEM-BSE image of: **a** phase precipitated on the internal wall of sample 203; **b** detail of the precipitated phase, with also the EDS analysis which shows its chemical composition

silica solution in hydrothermal conditions (120 °C) after 1 day of heating. A similar process could be responsible of the silica-rich crust in samples 203. It may represent the accumulation and deposition of silica from the boiling of plants. The tissue of some plants, in fact, is characterised by a microscopic structure composed of amorphous silica containing up to about 10% of water, namely phytoliths. The accumulation of these skeletal portions of amorphous silica from the processing of some plant through cooking, determined the formation of this crust of amorphous silica, then contaminated by other chemical elements circulating in solution in the fluid that permeated in the post-depositional environment. The transformation of this amorphous into a crystalline mineral phase/s was probably prevented by the short duration of the heating process with respect to the minimum time necessary to promote nucleation and growing [35].

Conclusions

The *tts*- μ XRD analysis on secondary phases in ancient pottery represents an important method to univocally define whether these phases are true minerals or amorphous precipitates. The small size of the focused spot ($15 \times 15 \mu\text{m}$) of *tts*- μ XRD allows to analyse small-size phases, often precipitated in submillimetric pores within the ceramic body, which cannot be mechanically separated. Other methods that allow local analysis, such as micro-Raman spectroscopy, could also be used to determine the mineralogical nature of these phases, although in some cases, when dealing with archaeological porous materials, micro-Raman may encounter fluorescence effects that add noise to the recorded experimental data. Besides that, the availability of XRPD databases containing thousands of mineral phases (PDF-type databases) almost guarantees to find adequate correspondences without the need to acquire experimental patterns from standard samples.

In this case study some mineral phases, the occurrence of which was previously defined only on chemical composition grounds either using scanning electron microscope [8] or electron microprobe [5, 6] analyses, have been now univocally identified as minerals whilst for others it has been shown that they precipitated as amorphous phases during the pots use or in the burial environment, although showing a chemical composition that sometimes is stoichiometrically consistent with that of specific mineral phase (mitridatite).

The *tts*- μ XRD, finally, seems to be an interesting analytical method in archaeological study, since the precise mineralogical definition allows to grasp functional aspects of prehistoric pottery assemblages that may otherwise remain obscured, as well as defining the post-depositional processes and conditions which determined

their formation. In the case of Al-Khiday Mesolithic specimens it provided a hint on some possible indications connected to the subsistence system of this group of hunter-gatherers on which it seems worth to investigate thoroughly.

The synchrotron through-the-substrate microdiffraction (*tts*- μ XRD) represent therefore a powerful method to determine univocally the mineralogical nature of small-sized remnants of secondary phases in pottery, but also in all kind of archaeological materials.

Additional file

Additional file 1: Figure S1. Pattern matching of vivianite phase (sample FRE48). Refined unit cell parameters: $a = 10.148(1)$ $b = 13.419(2)$ $c = 4.690(1)$ Å $\beta = 104.94(1)^\circ$. The experimental pattern (red dots) results from the integration of 8 2D X-ray diffraction frames (of 2 different microvolumes, 4 frames each). Calculated (black line), difference curve (bottom blue line) and Bragg reflection positions (green vertical lines) are shown in the plot. **Table S1.** List of Bragg reflections and their position after the pattern matching of vivianite (wavelength = 0.4246 Å). Refined unit cell parameters: $a = 10.148(1)$ $b = 13.419(2)$ $c = 4.690(1)$ Å $\beta = 104.94(1)^\circ$.

Abbreviations

EDS: energy dispersive X-ray spectrometry; EMPA: electron microprobe analysis; SEM: scanning electron microscope; SEM-BSE: scanning electron microscope-back scattered electron; *tts*- μ XRD: synchrotron radiation through-the-substrate microdiffraction; XRPD: X-ray powder diffraction.

Authors' contributions

LM, LC, AC, JR designed the research; LM and DU performed the sampling; LM and EG performed the microstructural analysis; LM, LC, AC, JR, OV performed the *tts*- μ XRD analysis; DU did the archaeological interpretation; all the authors contributed in the writing. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

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